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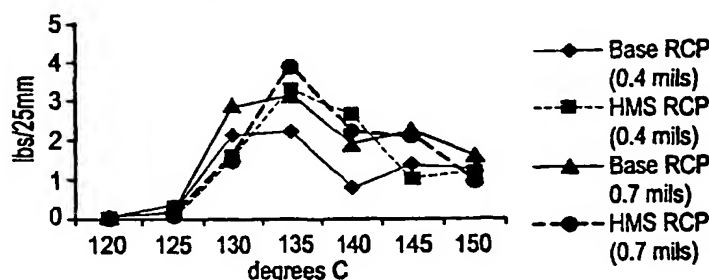
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[Continued on next page]

(54) Title: COMPOSITION AND FILMS THEREOF

Heat Seal Strength HMS PP Films



(57) Abstract: The present invention includes a composition comprising (a) at least one propylene polymer coupled by reaction with a coupling amount of poly(sulfonyl azide) sufficient to increase the melt strength of the propylene polymer before coupling at least 1.5 fold as compared with the resulting coupled propylene polymer; and (b) at least one ethylene polymer wherein the ethylene polymer is present in an amount sufficient to improve film mechanical properties of tear resistance in either the machine direction (MD) and cross direction (CD) as measured by the Elmendorf Tear method (ASTM D-1922) or dart impact strength as measured by the procedure of ASTM D-1709 or a modified method thereof in which the height from which the dart is dropped is decreased from 26" to 10.5" (0.66m to 0.27m) as compared with a film formed in the same manner using the coupled propylene polymer of (a) alone. Preferably, the propylene polymer is present in an amount of greater than 50 weight percent of the resulting composition and the ethylene polymer is present in an amount of from 5 to 49 weight percent. The invention also includes any blown film blown from a composition of the invention, particularly when blown on a high or low stalk extruder or coextruded as well as the process of blowing such a film. Further, the invention includes any article comprising a composition of the invention or comprising a film of the invention. Particular embodiments are those articles including an institutional liner, consumer liner, heavy duty shipping sack, produce bag, batch inclusion bag, pouch, grocery bag, merchandise bag, packaging, cereal liner, soft paper overwrap, multi-wall bag, lamination or combination thereof, including multiwall or multilayer configurations thereof. Further, the invention includes the use of a composition of the invention for making a blown film.

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COMPOSITION AND FILMS THEREOF

This invention relates to polyolefins, more particularly to propylene polymer compositions.

5

BACKGROUND

Currently, blown films are made predominantly from ethylene polymers. There are references to blowing films of propylene polymers, but none are observed to be commercially successful. The low melt strength of propylene polymers inhibits
10 production of blown film with such polymers at commercially feasible rates on standard equipment.

Scheve et al. in U.S. Patent 5,519,785 disclosed the use of polypropylenes having a branching index less than one and having a strain hardening elongational viscosity to blow certain films. The polymers were treated with radiation under
15 specified conditions in a multistep process which involves specialized equipment in steps after polymerization. Such a process is multi step, difficult and preferably avoided.

Giacobbe and Pufka in U.S. Patent 5,641,848 disclose making blown films from a propylene polymer material of broad molecular weight distribution (MWD of 4-60), a
20 melt flow rate of 0.5 to 50 dg/min. and xylene insolubles (at 25°C) of greater than or equal to 94 percent, said propylene polymer material selected from a broad molecular weight distribution propylene homopolymer and an ethylene propylene rubber impact modified broad molecular weight homopolymer. But this blend forms blown films at rates lower than those used commercially for polyethylene blown films.

25 In some instances, blowing films of polypropylene has been achieved by coextruding a polypropylene with another polymer. For instance, Nicola disclosed in DE 19650673 the use of a rubber modified polypropylene layer between polypropylene layers. Similarly, Landoni in EP 595252 disclosed the use of linear low density polyethylene or linear medium density polyethylene, optionally with added
30 hydrogenated hydrocarbon resins or other resins or low molecular weight polyethylene

or polypropylene waxes between external layers of polypropylene. In EP 474376, Schirmer et al. disclose the use of an ethylene vinyl acetate copolymer (EVA), very low density polyethylene (VLDPE) or ethylene alpha olefin copolymer with a broad molecular weight distribution with a polypropylene layer and a sealable layer. It would
5 be desirable to use monolayer films to provide the desired performance.

It would therefore be desirable to have a propylene polymer composition with sufficient melt strength to maintain a stable bubble for blown film manufacture on commercially available equipment, preferably that equipment available for the blowing of ethylene polymer compositions, more preferably both air and water quenched blown
10 film equipment in both high and low stalk configurations, that is equipment commonly used for high density and low density polyethylenes, respectively. The term "stalk" is used to designate the neck height of a bubble of polymer being blown into film. To achieve this end, a propylene polymer composition would advantageously have a melt strength that is higher than 10, preferably between 10-100 cN, more preferably between
15 20-80 cN, and most preferably between 25-75 cN (measured at 190 °C). Further, it is desirable that the resulting film shows at least a mechanical properties balance.

Rheology modification of the propylene polymers through reaction with coupling agents has now been found to improve the melt strength of the propylene polymers sufficiently to permit production of blown films with the rheology modified
20 propylene polymers at commercially acceptable rates.

As used herein, the term "rheology modification" means change in the resistance of the molten polymer to flow. The resistance of polymer melts to flow is indicated by (1) the tensile stress growth coefficient and (2) the dynamic shear viscosity coefficient. The tensile stress growth coefficient η_{E+} is measured during start-up of
25 uniaxial extensional flow by means within the skill in the art such as is described by J. Meissner in Proc. XIIth International Congress on Rheology, Quebec, Canada, August 1996, pages 7-10 and by J. Meissner and J. Hostettler, Rheol. Acta, 33, 1-21 (1994). The dynamic shear viscosity coefficient is measured with small-amplitude sinusoidal shear flow experiments by means within the skill in the art such as described by R.
30 Hingmann and B. L. Marczinke, J. Rheol. 38(3), 573-87, 1994.

SUMMARY OF THE INVENTION

In one embodiment, the present invention includes a composition comprising (a) at least one propylene polymer coupled by reaction with a coupling amount of
5 poly(sulfonyl azide) sufficient to increase the melt strength of the coupled propylene polymer to at least 1.5, preferably 3, fold that of the propylene polymer before coupling; and (b) at least one ethylene polymer, wherein the ethylene polymer is present in an amount sufficient to improve film mechanical properties (of a blown film of the composition) of tear resistance in either the machine direction (MD) or cross
10 direction (CD) as measured by the Elmendorf Tear method (ASTM D-1922) or dart impact strength as measured by the procedures of ASTM D-1709 or a modified method thereof in which the height from which the dart is dropped is decreased from 26" to 10.5" (0.66m to 0.27m) as compared with a film formed in the same manner using the coupled propylene polymer of (a) alone. Preferably, the propylene polymer is present
15 in an amount of greater than 50 weight percent of the resulting composition and the ethylene polymer is present in an amount of from 5 to 49 weight percent. The invention also includes any film blown from a composition of the invention, particularly when blown on a high or low stalk extruder or coextruded as well as the process of blowing such a film. Further, the invention includes any article comprising a
20 composition of the invention or comprising a film of the invention.

In a second embodiment the invention is a coextruded film comprising (a) at least one layer comprising at least one coupled propylene polymer coupled by reaction with a poly(sulfonyl azide) to increase the melt strength of the coupled propylene polymer to at least 1.5 fold that of the propylene polymer before coupling; and (b) at
25 least one layer comprising at least one ethylene polymer.

Particular embodiments are those articles including an institutional liner, consumer liner, heavy duty shipping sack, produce bag, batch inclusion bag, pouch, grocery bag, merchandise bag, packaging, cereal liner, soft paper overwrap, multi-wall bag, lamination or combination thereof, including multiwall or multilayer

configurations thereof. Further, the invention includes the use of a composition of the invention for making a blown film.

BRIEF DESCRIPTION OF THE FIGURES

5 Figure 1 is a diagram showing the heat seal strength versus temperature of 0.4 mil and 0.7 mil films made from coupled and uncoupled random propylene copolymers.

Figure 2 is a bar chart showing the back pressure present during the processing of a coupled propylene impact copolymer and a high molecular weight high density
10 polyethylene polymer on a linear low density polyethylene blown film processing line.

Figure 3 is a bar chart showing the maximum output rates for several polymers on a linear low density polyethylene blown film processing line.

DETAILED DESCRIPTION OF THE INVENTION

15 As used herein, "coupling" refers to modifying the rheology of a polymer by reacting the polymer with a suitable coupling agent. A "coupled polymer" is a rheology modified polymer resulting from a coupling reaction. A coupled polymer is characterized by an increase in melt strength of at least 25 percent and a decrease in melt flow rate (MFR), compared to the polymer before coupling. A coupled polymer
20 differs from a crosslinked polymer in that the coupled polymer is thermoplastic and has a low gel level. In contrast, crosslinking (otherwise known as "vulcanization") results in a thermoset polymer characterized by high gel levels.

Crosslinking is evidenced by gel formation which is measured in the case of polypropylene by xylene insolubility, or in the case of films by optically evident gels in
25 a film, for instance as analyzed by a laser gel counter commercially available from Optical Control System, Inc. under the trade designation FS-3

The term "a coupling amount" of poly(sulfonyl azide) is used herein to designate that amount of poly(sulfonyl azide) effective to result in a measurable increase in melt strength of the polymer it reacts with such that the desired or
30 predetermined amount of modification is realized.

"Melt Strength" is measured by using a capillary rheometer fitted with a 2.1 mm diameter, 20:1 die with an entrance angle of approximately 45 degrees. After equilibrating the samples at 190°C for 10 minutes, the piston is run at a speed of 1 inch/minute. The standard test temperature is 190°C. The sample is drawn uniaxially to a set of accelerating nips located 100 mm below the die with an acceleration of 2.4 mm/sec². The required tensile force is recorded as a function of the take-up speed of the nip rolls. The maximum tensile force attained during the test is defined as the melt strength. In the case of polymer melt exhibiting draw resonance, the tensile force before the onset of draw resonance was taken as melt strength. The melt strength is recorded in centiNewtons.

The term "mechanical properties balance" is used to mean good toughness as measured by tear strength greater than 5 g/mil in machine direction (MD) and 20 g/mil in cross direction (CD).

A propylene polymer (also called polypropylene) is any polymer comprising greater than sixty (60) weight percent, preferably, greater than sixty five (65) weight percent -CHCH₃CH₂- repeating units as derived from a propylene monomer. Propylene polymers include propylene homopolymer as well as random and impact copolymers of propylene. Such polymers include terpolymers, tetrapolymers and higher order polymers of ethylene, propylene and other olefins optionally dienes.

An ethylene polymer is any polymer comprising greater than fifty weight percent -CH₂CH₂- repeating units as derived from an ethylene monomer. Ethylene polymers include homopolymers of ethylene as well as random and block copolymers of ethylene. Such polymers include terpolymers, tetrapolymers and higher order polymers of ethylene, propylene and other olefins optionally dienes.

PROPYLENE POLYMERS

This invention involves compositions of at least one propylene polymer which is coupled using a poly(sulfonyl azide) and at least one ethylene polymer.

In either propylene copolymers or ethylene copolymers, the propylene or ethylene, respectively, is suitably copolymerized with one or more monomers copolymerizable therewith, but preferably with at least one other olefin or alpha olefin.

Olefins include ethylene and alpha olefins, which include propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-nonene, 1-decene, 1-undecene, and 1-dodecene as well as 4-methyl-1-pentene, 4-methyl-1-hexane, 5-methyl-1-hexane, vinylcyclohexane, and styrene. Preferred olefins and alpha olefins for copolymerization with propylene
5 include ethylene, butylene, and other higher alpha olefins, that is alpha olefins having at least 3 carbon atoms, more preferably ethylene or butylene, and higher alpha olefins, most preferably ethylene. Preferred alpha olefins for copolymerization with ethylene include propylene, butene, pentene, hexene, heptene, and octene, more preferably hexene or octene, most preferably octene.

10 The polymer starting materials are suitably of any molecular weight distribution (MWD). MWD is calculated as the ratio M_w/M_n , where M_w is the weight average molecular weight and M_n is the number average molecular weight. Those skilled in the art are aware that polymers having a MWD less than 3 are conveniently made using a metallocene or constrained geometry catalyst (especially in the case of ethylene
15 polymers) or using electron donor compounds with Ziegler Natta catalysts (especially in the case of polypropylene). In the practice of the invention, the MWD is preferably at least 2 and more preferably up to 8, most preferably up to 5.

Polyolefins are formed by means within the skill in the art. The alpha olefin monomers and optionally other addition polymerizable monomers are polymerized
20 under conditions within the skill in the art, for instance as disclosed by Galli, et al., Angew. Macromol. Chem., Vol. 120, p. 73 (1984), or by E. P. Moore, Propylene Handbook, Hanser, New York, 1996 pages 15-45, 74-111, U.S. Patents 3,645,992; 3,687,920; 3,893,989; 3,914,342; 4,003,712; 4,076,698; 4,113,802; 5,272,236; 5,278,272; 5,747,594; 5,844,045 and 5,869,575.

25 The comonomers or combination of comonomers is used in any relative quantities within the definitions of the polymers. For propylene polymers, the comonomer content is preferably less than 35, more preferably 2-30, most preferably 5-20 weight percent.

The propylene polymers are preferably stereoregular (that is syndiotactic or isotactic), more preferably isotactic, most preferably having an isotacticity as measured by C^{13} NMR of at least 50 percent .

The propylene polymer melt flow rate is measured by ASTM D1238L at
5 230°C/2.16 kg. The melt flow rate is preferably at least 0.1, more preferably at least 0.2 g/10 min. It is preferably up to 20, more preferably up to 10, most preferably up to 4 g/10 min. to achieve good processability and mechanical properties balance. One recognizes good processability by high output rates (>6 pounds per hour per inch of die circumference (0.298 g/s/cm)).

10 The propylene polymer is advantageously a homopolymer for purposes of ready availability of starting material and resulting competitive pricing. Random and impact copolymers are preferred for compatibility of propylene and ethylene polymers. Higher compatibility results in improved film physical and mechanical properties such as tear and dart as compared with the base polypropylene resin of the copolymers, impact
15 copolymers are more preferred, again, because they are very compatible with ethylene copolymers. Random copolymers are preferred when film optical properties (that is clarity and haze) are important.

Impact propylene copolymers are commercially available and are well within the skill in the art, for instance, as described by E.P. Moore, Jr in Polypropylene
20 Handbook, Hanser Publishers, 1996, page 220 and U.S. Patents 3,893,989 and 4,113,802. The term "impact copolymer" is used herein to refer to heterophasic propylene copolymers where polypropylene is the continuous phase and an elastomeric phase is uniformly dispersed therein. The impact copolymers result from an in-reactor process rather than physical blending. Usually the impact copolymers are formed in a
25 dual or multi-stage process, which optionally involves a single reactor with at least two process stages taking place therein, or optionally multiple reactors. Advantageously, the impact copolymers have at least 5 weight percent, preferably at least 10, preferably up to 40, more preferably up to 25 weight percent, and most preferably up to 20 weight percent ethylene. Illustrative impact copolymer propylene polymers include those
30 available from The Dow Chemical Company under the trade designations INSPiRE

C104-01, INSPiRE C105-02, DC-111, and INSPiRE C107-04, propylene impact copolymers having melt flow rates of 1, 2, 0.8, and 4 g/10 min, respectively, under a weight of 2.16 kg at a temperature of 230°C and flexural (flex) modulus as measured according to the procedures of ASTM D 790A of 180,000, 140,000, 166,800, and
5 170,000 psi (1,241,056; 965,266; 1,150,000, and 1,172,109 kPa, respectively).

COUPLING AGENTS

In the practice of the invention, at least one propylene polymer resin is reacted with a chain coupling agent which is a poly(sulfonyl)azide. When the poly(sulfonyl)azide reacts with the propylene polymer resin, at least two separate
10 propylene polymer chains are advantageously joined and the molecular weight of the polymer chain is increased. In the preferred case when the poly(sulfonyl azide) is a bis(sulfonyl azide) (hereinafter "BSA"), two propylene polymer chains are advantageously joined.

The poly(sulfonyl azide) is any compound having at least two sulfonyl azide
15 groups ($-\text{SO}_2\text{N}_3$) reactive with the propylene polymer. Preferably the poly(sulfonyl azide)s have a structure $\text{X}-\text{R}-\text{X}$ wherein each X is SO_2N_3 and R represents an unsubstituted or inertly substituted hydrocarbyl, hydrocarbyl ether or silicon-containing group, preferably having sufficient carbon, oxygen or silicon, preferably carbon, atoms to separate the sulfonyl azide groups sufficiently to permit a facile reaction between the
20 propylene polymer and the sulfonyl azide, more preferably at least 1, more preferably at least 2, most preferably at least 3 carbon, oxygen or silicon, preferably carbon, atoms between functional groups. While there is no critical limit to the length of R, each R advantageously has at least one carbon or silicon atom between X's and preferably has less than 50, more preferably less than 20, most preferably less than 15 carbon, oxygen
25 or silicon atoms. Silicon containing groups include silanes and siloxanes, preferably siloxanes. The term inertly substituted refers to substitution with atoms or groups which do not undesirably interfere, at the coupling reaction conditions, with the desired reaction(s) or desired properties of the resulting coupled polymers. Such groups include fluorine, aliphatic or aromatic ether, siloxane as well as sulfonyl azide groups
30 when more than two propylene polymer chains are to be joined. R is suitably aryl,

alkyl, aryl alkaryl, arylalkyl silane, siloxane or heterocyclic, groups and other groups which are inert and separate the sulfonyl azide groups as described. More preferably R includes at least one aryl group between the sulfonyl groups, most preferably at least two aryl groups (such as when R is 4,4' diphenylether or 4,4'-biphenyl). When R is one aryl group, it is preferred that the group have more than one ring, as in the case of naphthylene bis(sulfonyl azides). Poly(sulfonyl)azides include such compounds as 1, 5-pentane bis(sulfonylazide), 1,8-octane bis(sulfonyl azide), 1,10-decane bis(sulfonyl azide), 1,10-octadecane bis(sulfonyl azide), 1-octyl-2,4,6-benzene tris(sulfonyl azide), 4,4'-diphenyl ether bis(sulfonyl azide), 1,6-bis(4'-sulfonazidophenyl)hexane, 2,7-naphthalene bis(sulfonyl azide), and mixed sulfonyl azides of chlorinated aliphatic hydrocarbons containing an average of from 1 to 8 chlorine atoms and from 2 to 5 sulfonyl azide groups per molecule, and mixtures thereof. Preferred poly(sulfonyl azide)s include oxy-bis(4-sulfonylazidobenzene), 2,7-naphthalene bis(sulfonyl azido), 4,4'-bis(sulfonyl azido)biphenyl, 4,4'-diphenyl ether bis(sulfonyl azide) and bis(4-sulfonyl azidophenyl)methane, and mixtures thereof.

Sulfonyl azides are commercially available or are conveniently prepared by the reaction of sodium azide with the corresponding sulfonyl chloride, although oxidation of sulfonyl hydrazines with various reagents (nitrous acid, dinitrogen tetroxide, nitrosonium tetrafluoroborate) has been used.

The subject matter of this invention is not dependent on the reaction mechanisms. The following discussion regarding the coupling reaction mechanism provides the inventors current theories but is not intended to limit the scope of this invention. Sulfonyl azides decompose in several ways, but for the practice of the invention, the reactive species, believed to be the singlet nitrene, as evidenced by insertion into C-H bonds is desired. Thermal decomposition is reported to give an intermediate singlet sulfonyl nitrene, which will react readily by insertion into carbon-hydrogen bonds. The high temperatures necessary for efficient formation of the sulfonyl nitrene is usually greater than 150°C. Sulfonyl azides also form another intermediate believed to be a triplet nitrene under appropriate conditions, such as

temperatures in excess of 250 °C. This intermediate leads to chain scission and, therefore, is preferably avoided in the practice of this invention.

The poly(sulfonyl azide) is preferably at least partially mixed with the propylene polymer before the resulting mixture is heated to the peak decomposition temperature of the poly(sulfonyl azide). By peak decomposition temperature of the poly(sulfonyl azide) is meant that temperature at which the azide converts to the sulfonyl nitrene, eliminating nitrogen and more heat in the process. Specifically the peak decomposition temperature, as determined by differential scanning calorimetry (DSC). For instance, a differential scanning calorimeter (DSC) thermogram of the bis (sulfonyl azide) of diphenyl oxide shows a no change in the heat flow until a sharp endothermic melting peak is observed at 100 °C. The baseline is flat again (no heat flow) until a broad exothermic peak is observed that begins about 150 °C, peaks at 185 °C (referred to herein as the peak decomposition temperature) and is complete by 210 °C. The total amount of energy released due to decomposition of the sulfonyl azide groups is about 1500 Joules/gram. The peak decomposition temperature is advantageously greater than 150 °C, preferably greater than 160 °C, more preferably greater than 180 °C.

Those skilled in the art recognize that reactivity, the poly(sulfonyl)azide and the desired or predetermined amount of chain coupling determine the amount of poly(sulfonyl)azide to be used. In the compositions of the invention, the amount of coupling desirable is optionally determined from the desired melt strength in the coupled propylene polymer. The melt strength of the coupled propylene polymer is advantageously sufficient for the propylene polymer/ethylene polymer blend to form and maintain a sufficiently stable bubble on film blowing equipment to run at commercial output rates. Preferably, the melt strength of the coupled propylene polymer is at least 5, more preferably at least 10 cN. To avoid blown film bubble instabilities, the melt strength is preferably up to 100, more preferably up to 75 cN. Determining the amount of poly(sulfonyl azide) that gives this result is within the skill in the art. The amount is preferably at least 50 parts per million by weight of the propylene polymer (ppm), more preferably at least 100 ppm, most preferably at least

150 ppm and, in some instances, preferably at least 200 ppm. In the practice of the invention, formation of crosslinked networks to an extent that would result in intractable propylene polymer is to be avoided; therefore, poly(sulfonyl azide) is preferably limited to that amount which results in chain coupled or rheology modified
5 (but not substantially crosslinked) propylene polymer, preferably less than 1000 ppm, more preferably less than 600 ppm, most preferably less than 500 ppm poly(sulfonyl azide) based on the total weight of propylene polymer, preferably polypropylene or polypropylene/ethylene copolymer blend. Substantial crosslinking is characterized by the presence of gels of sufficient size or weight percentage such that the processing of
10 the film is detrimentally affected. Such detrimental effects include output reduction; discontinuity of the film; increased backpressure; and/or, partial die plugging.

PREPARATION OF MODIFIED POLYPROPYLENE

The propylene polymer(s) and coupling agent are suitably combined in any
15 manner which results in desired reaction thereof, preferably by mixing the coupling agent with the polymer under conditions which allow sufficient mixing before or during reaction to avoid unnecessary or undesirably uneven amounts of localized reaction. An undesirable amount is an amount which interferes with the purpose of the final product. Any mixing equipment is suitably used with the invention, preferably equipment which
20 provides sufficient mixing and temperature control in the same equipment, but advantageously practice of this embodiment takes place in such devices as an extruder, melt mixer, pump conveyor or a polymer mixing devise such as a Brabender melt mixer. While it is within the scope of this embodiment that the reaction take place in a solvent or other medium, it is preferred that the reaction be in a bulk phase to avoid
25 later steps for removal of the solvent or other medium. In a preferred embodiment the process of the present invention takes place in a single vessel, that is mixing of the coupling agent and polymer takes place in the same vessel as heating to the decomposition temperature of the coupling agent. The vessel is most preferably a twin-screw extruder, but preferably a single-screw extruder or advantageously a melt mixer,

including a batch mixer. The reaction vessel more preferably has at least two zones of different temperatures into which a reaction mixture would pass.

In the most preferred embodiment, the propylene polymer and the coupling agent are physically mixed at a temperature which is low enough to minimize the reaction between the coupling agent and the polymer. Such physical mixing can occur in any equipment, such as V-blenders, ribbon or paddle blenders, tumbling drums, or extruders, which will mix the coupling agent and the propylene polymer. The term extruder is used for its broadest meaning to include such devices as a device which extrudes pellets as well as an extruder which produces the extrudate for forming into articles, such as a film.

Preferably, this physical mixing occurs in the early stages of an extruder, most preferably a twin screw extruder. In particular, this embodiment may be practiced by simultaneously introducing the propylene polymer resin and the coupling agent into the feed section of an extruder. The extruder is configured to have a first section that physically mixes and conveys the coupling agent and polymer in a manner that minimizes the reaction between the coupling agent and the polymer. The melt stream temperature(s) in the first section are preferably less than 180 C, more preferably less than 170 C, most preferably less than 140 C, and in some instances less than 130 C, preferably less than 120 C. The conveying first section is followed by at least a second section where the coupling agent and polymer are rapidly further mixed and sufficient heat is added to cause significant reaction between the coupling agent and polymer. Preferably, the melt stream temperature(s) in the second section are from 160 C to 250 C, more preferably from 200 C to 250 C, in order to obtain sufficient reaction between the coupling agent (poly(sulfonyl azide)) and the propylene polymer. Where degradation of the propylene polymer is of a particular concern, the melt stream temperature is preferably from 200 C to 230 C.

In the description of this invention, when temperatures are described in terms of the stream temperatures, that is, temperatures inside the polymer stream or polymer melt rather than the temperatures of the equipment, which are understood by those skilled in the art to be likely to be lower or higher than stream temperatures because of

imperfect heat transfer into the polymer or induced shear heating of the polymer.

Those skilled in the art can determine the relationship between stream temperature and equipment or gage temperature of particular equipment without undue experimentation.

It is known in the art that the polymer melt (stream) temperature is advantageously

5 close to the machine set temperature in the initial zones of an extruder, but the polymer melt (stream) temperature can often be greater than the machine set temperatures in the latter zones of the extruder as it approaches the exit die of the extruder due to mechanically induced shear heating.

In another embodiment, the mixing is preferably attained with the polymer in a
10 molten or at least partially melted state, that is, above the softening temperature of the polymer, or in a dissolved or finely dispersed condition rather than in a solid mass or particulate form. Melt phase mixing is advantageous for forming a substantially uniform admixture of coupling agent and polymer before exposure to conditions in which a significant amount of chain coupling takes place. Conveniently for this
15 embodiment, the formation of a substantially uniform admixture occurs along a temperature profile within equipment such as an extruder. The first zone is advantageously at a temperature at least the softening temperature of the polymer(s) and preferably less than the decomposition temperature of the coupling agent s and the second zone being at a temperature sufficient for decomposition of the coupling agent.
20 Especially in the case of propylene polymers, most preferably the propylene polymer(s) and coupling agent are exposed to a profile of melt stream temperatures ranging from 160 °C to 250 °C.

Those skilled in the art recognize that a polymer, or mixture thereof, typically melts over a range of temperatures rather than melting sharply at one temperature. For
25 the practice of this embodiment, it is sufficient that the polymer be in a partially melted state. For convenience, the temperature of this degree of melting can be approximated from the differential scanning calorimeter (DSC) curve of the polymer or mixture thereof to be treated.

Conveniently, when there is a melt extrusion step between production of the
30 polymer and its use, at least one step of the process of the invention takes place in the

melt extrusion step. The heat produced during the extrusion step provides the energy necessary to cause the reaction between the coupling agent and the target polymer.

For all embodiments, a temperature of at least the decomposition temperature of the coupling agent is preferably maintained for a time sufficient to result in
5 decomposition of at least sufficient coupling agent to avoid later undesirable reaction, preferably at least 80, more preferably at least 90, most preferably at least 95 weight percent of the coupling agent is reacted. Those skilled in the art realize that this time is dependent on whether the temperature is one at which the coupling agent slowly decomposes or one at which it very rapidly decomposes. Preferably, the time will be at
10 least 5 seconds, more preferably at least 10 seconds to avoid unreacted coupling agent, and subsequent undesirable reactions, or to avoid the need for inconveniently, possible destructively high temperatures. Conveniently, the reaction time is 20 seconds.

As discussed previously, the melt strength of the propylene polymer is advantageously increased by this coupling reaction. Preferably, the melt strength is
15 increased to at least 1.5, more preferably 2.0, times the melt strength of the polypropylene before coupling, most preferably at least 3 times that of the polymer before coupling and in some instances at least 11 times that of the polymer before coupling. The melt strength is preferably at least sufficient to support a stable bubble at output rates of at least 6 lb/hr/in of die circumference (0.298 g/s/cm) at 2 mil (50
20 micron) gauge, more preferably at least 8 lb/hr/in of die circumference (0.397 g/s/cm) at 2 mil gauge, most preferably at least 11 lb/hr/in of die circumference (0.546 g/s/cm) at 2 mil gauge, and, in some instances, at least 14 lb/hr/in of die circumference (0.695 g/s/cm) at 2 mil gauge. Preferably, the melt strength of modified propylene polymer is up to 20 times that of the polymer before coupling, more preferably 12 or less. When
25 excessive levels of coupling agents are used, one can experience gels, poor drawability (insufficient to draw the film to gauges as low as 0.6 mils (15 microns)), tear-off at the die, and lower than desired mechanical properties, such as dart and tear strength.

Melt strength is measured in uniaxial conditions extensional flow at isothermal conditions. Linear chains of isotactic polypropylene do not strain harden for all
30 molecular weights reported in literature. In contrast, homopolymer and random

copolymer chain-coupled isotactic polypropylene chains strain harden strongly as indicated by a rise in the viscosity η_{E+} by a factor of 10-100 when characterized under the same conditions. Surprisingly, the impact copolymer polypropylene resins used by us do not strain harden on coupling when characterized under the same condition.

5

ETHYLENE POLYMERS

The modified polypropylene may be blended with various ratios of at least one ethylene polymer, preferably linear low density polyethylene (LLDPE), substantially linear polyethylene, or a homogeneously branched linear polyethylene, to provide enhanced mechanical properties. Optionally, but not in the most preferred embodiment, the ethylene polymers have monomers having at least two double bonds which are preferably dienes or trienes. Suitable diene and triene comonomers include 7-methyl-1,6-octadiene, 3,7-dimethyl-1,6-octadiene, 5,7-dimethyl-1,6-octadiene, 3,7,11-trimethyl-1,6,10-octatriene, 6-methyl-1,5-heptadiene, 1,3-butadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, norbornene, tetracyclododecane, or mixtures thereof, preferably butadiene, hexadienes, and octadienes, most preferably 1,4-hexadiene, 4-methyl-1,4-hexadiene, 5-methyl-1,4-hexadiene, dicyclopentadiene, and 5-ethylidene-2-norbornene. These monomers are optionally used with ethylene alone or, preferably, with ethylene and at least one additional monomer polymerizable therewith, most preferably propylene as in the case of ethylene/ propylene/ diene rubber (EPDM). The comonomer content is preferably less than 50, more preferably 2-30, most preferably 5-20 weight percent.

The polymer starting materials are suitably of any molecular weight distribution (MWD). MWD is calculated as the ratio M_w/M_n , where M_w is the weight average molecular weight and M_n is the number average molecular weight. Those skilled in the art are aware that polymers having a MWD less than 3 are conveniently made using a metallocene or constrained geometry catalyst (especially in the case of ethylene polymers) or using electron donor compounds with Ziegler Natta catalysts (especially in the case of polypropylene). In the practice of the invention, the MWD is preferably at least 2 and more preferably up to 8, most preferably up to 5.

The ethylene polymers preferably have a melt index (MI) as measured by ASTM D-1238 condition 190°C/2.16 Kg (formerly known as Condition E) sufficient to support a 2 mil (50 micron) blown film bubble, preferably at least 0.1 g/10 min., more preferably at least 0.5 g/10 min. The MI is preferably less than 15, more preferably less than 10, most preferably less than 6 g/10 min.

The ethylene polymers preferably have a density at least 0.865 g/cm³ as measured by ASTM D 792, more preferably at least 0.87 g/cm³, most preferably at least 0.88 g/cm³. Preferably, the density is less than 0.96, more preferably up to 0.95, most preferably up to 0.930 g/cm³. Most preferably, the ethylene polymer is linear low density polyethylene (LLDPE), a substantially linear polyethylene, or a homogeneously branched linear polyethylene. Substantially linear polyethylene is that polyethylene described in U.S. Patents 5,373,236 and 5,278,272. Examples of a homogeneously branched linear polyethylene are polyethylenes having a CDBI greater than 50 percent as calculated in accordance with WO 93/ 04486 using the equipment and procedures as described in U. S. Patent No. 5,008,204, such as polyethylenes available from the Exxon Chemical Company under the trade names EXCEED and EXACT. Ethylene polymers suitable for practice of the invention include polymers such as those commercially available from The Dow Chemical Company under the trade designations DOWLEX, AFFINITY and ELITE polyethylenes; polymers commercially available from Exxon Chemical Corporation under the trade designation EXACT and EXCEED and polymers commercially available from Mitsui Petrochemical Industries under the trade designation TAFMER. More specifically preferred polyethylenes include such polymers as polyethylene commercially available from The Dow Chemical Company under the trade designation DOWLEX 2045 polymer and polyethylene commercially available from Equistar, Inc. under the trade designation Petrothene GA501020 polymer.

In an alternative embodiment, the polyethylene is preferably a high density polyethylene, more preferably having a density of at least 0.940 g/cm³. Most preferably the density is between 0.940 and 0.962 g/cm³, inclusively. The high density polyethylene preferably has a molecular weight at least 100,000 and is of the type

referred to in the art as high molecular weight, high density polyethylene (HMWHDPE). More preferably the molecular weight is between 150,000-300,00 inclusively. Such polyethylenes are within the skill in the art, for instance, as commercially available from Equistar, Inc. under the trade designation HDPE 5005
5 polymer or from The Dow Chemical Company under the trade designation High Density Polyethylene 53050E.

Melt or dry blending, for example at the hopper of the extruder or in an off-line tumble blending operation, is useful to achieve the blends of the invention. The ethylene polymer is advantageously observed to increase the film properties such as
10 tear resistance in both the machine direction (MD) and cross direction (CD) as measured by Elmendorf Tear (ASTM D-1922), dart impact as measured by ASTM D-1709 or a modified method thereof in which the height from which the dart falls is decreased from 26" to 10.5" (0.66m to 0.27m) as compared with a film formed in the same manner using the coupled propylene polymer(s) alone. Preferably, a sufficient
15 amount of ethylene polymer is used to increase at least one of the film properties of a film made of the blend by at least 20 percent, more preferably by at least 50 percent, most preferably by at least 100 percent compared with the film properties of a film formed in a similar manner using the coupled propylene polymer alone.

Preferably, the amount of ethylene polymer is at least 5 percent, more preferably
20 10 percent, most preferably at least 15 percent of the resulting blend of coupled polypropylene and polyethylene. At amounts of ethylene polymer of preferably less than 50 percent, more preferably less than 40 percent, most preferably less than 35 percent or less, films of acceptable stiffness can advantageously be obtained at relatively low cost. An acceptable film stiffness is a stiffness measured by secant
25 modulus (ASTM D882) sufficient to allow feeding of film into bag making equipment at convenient and acceptable rates by one skilled in the art.

In the alternative embodiment where high molecular weight, high density polyethylene is admixed with the coupled polypropylene, the polyethylene is preferably used in an amount corresponding to at least 5 percent by weight, more preferably at
30 least 10 weight percent, most preferably at least 15 weight percent of the resulting

blend. The polyethylene is used to increase the tear resistance of a film made from the blend as compared to that of a film made from the polypropylene alone. The amount of polyethylene is preferably less than 40, most preferably less than 30 weight percent of the resulting blend with the coupled polypropylene. As compared to the use of a lower
5 density polyethylene, use of the same amount of a high density, high molecular weight polyethylene in a blend with the same proportion of coupled polypropylene results in a film having higher modulus as measured according to the procedures of ASTM 882.

Those skilled in the art will recognize that more than one ethylene polymer is optionally used, particularly when each polymer contributes a desirable characteristic to
10 the blend or resulting film or other article. Similarly, more than one propylene polymer is optionally included in a blend of the invention. At least one of the propylene polymers is coupled in the practice of the invention; however, coupling of one or more other polymers included in the blend is optional. Furthermore, polymers other than ethylene polymers and propylene polymers are optionally included with the at least one
15 coupled propylene polymer and at least one ethylene polymer in blends of the invention.

FILM FORMING

Compositions of the invention are advantageously useful in making films, especially blown films. The technique of blown film extrusion is well known for the
20 production of thin plastic films. In an advantageous process, plastics, such as low, linear low, and high density polyethylene (LDPE, LLDPE, and HDPE) are extruded through a circular die to form a film. Air is introduced through the center of the die to maintain the film in the form of a bubble which increases the diameter of the film 2 to 6
25 fold, after which the bubble is collapsed onto rollers. There are a number of variations of such a process within the skill in the art, for instance as described in such references as U.S. Patents 3,959,425; 4,820,471, where the difference between high (referred to as "long stalk" therein) and low stalk film blowing is discussed at column 1; 5,284,613; W.D. Harris, et al in "Effects of Bubble Cooling on Performance and Properties of
30 HMW-HDPE Film Resins", Polymers, Laminations & Coatings Conference, Book 1,

1990, pages 306-317; and, Moore, E.P., Polypropylene Handbook, Hanser, New York, 1996, pages 330-332. Most references to blowing polyolefin films disclose processes used for polyethylene, but these are applicable to the blends of the invention with few modifications within the skill in the art without undue experimentation. For instance,
5 cooling is often advantageously modified because the art recognizes that polypropylene cools and crystallizes at a rate different from that of polyethylene. Therefore, adjustments to the cooling parameters often produce a more stable bubble at desired output rates.

In the formation of blown films, a melt enters a ring-shaped die either through
10 the bottom or side thereof. The melt is forced through spiral grooves around the surface of a mandrel inside the die and extruded through the die opening as a thick-walled tube. The tube is expanded into a bubble of desired diameter and correspondingly decreased thickness as previously described.

Two primary types of blown film equipment are of particular interest for
15 making films of the invention. One type is identified in the art with the making of low density and linear low density polyethylene films. This type is characterized by low stalk height (die to frost line distance of 2-6 die diameters), and a single screw extrusion using an annular die with die gaps measuring from 30-120 mils (750 – 3050 microns). This equipment is particularly useful for polymers having characteristics of: (a) higher
20 melt strength, that is melt strength above 1cN; (b) good drawability, that is the ability to be stretched to as thin as 0.5 mils (13 microns); and, (c) good processability, that is the ability to maintain a stable bubble at outputs rates of greater than 10 lbs/hr/inch (0.496 g/s/cm) of die circumference. Examples of equipment used in this process are produced by Battenfeld Gloucester, Inc., Davis-Standard Equipment, or Black-Clawson.

25 A second type of equipment is identified in the art with the making of high molecular weight high density polyethylene films. This type is characterized by a high stalk height (die to frost line distance of 5-15 die diameters). This equipment is particularly useful for polymers having characteristics of high molecular weight (that is melt index (I5) less than 0.5 g/10 minutes at 190°C and 5 kg), and a need for longer

cooling and relaxation times than LLDPE. Examples of this type of equipment are produced by Alpine, Inc. or Kiefel.

Surprisingly, blown films of the invention are advantageously produced on both high and low stalk types of equipment.

5 Preferably, compositions of the invention are optionally blown on the first type of equipment (that is, low stalk) at rates of at least 6 lb/hr/in of die circumference (0.298g/s/cm of die circumference), more preferably at least 8 lb/hr/in of die circumference (0.496 g/s/cm of die circumference), most preferably at least 10 lb/hr/in of die circumference (0.695 g/s/cm of die circumference).

10 The second type of film blowing equipment (that is, high stalk) is commonly used for blowing films from high molecular weight-high density polyethylene (that is polyethylene having a melt index (I_2), of at least 0.5 g / 10 min and a density of at least 0.940 g/ml).

15 The formation of coextruded blown films is known in the art and applicable to the present invention. Articles illustrative of the art include Han and Shetty, "Studies on Multilayer Film Coextrusion III. The Rheology of Blown Film Coextrusion," Polymer Engineering and Science, February, (1978), vol. 18, No. 3 pages 187-199; and Morris, "Peel Strength Issues in the Blown Film Coextrusion Process," 1996 Polymers, Laminations & Coatings Conference, TAPPI Press, Atlanta, Ga. (1996), pages 571-577.

20 The term "coextrusion" refers to the process of extruding two or more materials through a single die with two or more orifices arranged such that the extrudates merge together into a laminar structure, preferably before chilling or quenching. Coextrusion systems for making multilayer films employ at least two extruders feeding a common die assembly. The number of extruders is dependent upon the number of different
25 materials comprising the coextruded film. For each different material, a different extruder is advantageously used. Thus a five-layer coextrusion may require up to five extruders although less may be used if two or more of the layers are made of the same material.

30 Coextrusion dies are used to form coextruded blown films. They have multiple mandrels that feed the different melt streams to the circular die lip. When feedblocks

are employed to stack melt layers from two or more extruders, the resulting multilayered melt stream is then fed to the film die.

Coextruded blown films of the present invention can be formed into pouches, bags, and containers using packaging machinery within the skill in the art such as heat sealing devices using mandrels. Pouches, bags and other containers made from this combination of materials provide excellent toughness and impact strength and furthermore provide an excellent barrier to grease and oil and light hydrocarbons such as turpentine. Coextruded blown film of the present invention can be used as a packaging substrate alone, as a liner in multi-wall bags, or a strength/sealant ply in laminated structures such as with polyethylene terephthalate or biaxially oriented polypropylene.

In multilayer films each layer advantageously imparts a desired characteristic such as weatherability, heat seal, adhesion, chemical resistance, barrier layers (for example to water or oxygen), elasticity, shrink, durability, hand and feel, noise or noise reduction, texture, embossing, decorative elements, impermeability, and stiffness. Adjacent layers are optionally directly adhered, or alternatively have an adhesive, tie or other layer between them, particularly for the purpose of achieving adhesion therebetween. Constituents of the layers are selected to achieve the desired purpose.

In one aspect of the invention where toughness, optics, and/or heat seal performance are important, coextruded films employing a propylene polymer coupled using poly(sulfonyl azide) in one layer of such a multilayer film and an ethylene polymer is used in at least one other layer. The ethylene polymer layer will improve the overall toughness of the film structure. The coupled propylene polymer may comprise an impact copolymer, a random copolymer or a homopolymer of propylene. The polymer blends previously described and described hereinafter for use in monolayer films, may be used for one layer of a multilayer film. It is believed that ethylene polymers blended with the coupled propylene polymer will improve the compatibility of the propylene polymer and the ethylene polymer film layers for one another in the multilayer film structure. The ethylene polymer may comprise LLDPE, LDPE, HDPE, substantially linear polyethylene, homogeneously branched linear

polyethylene, and blends thereof. In one preferred aspect of the invention, a three layer film structure is used with a coupled propylene polymer, as described herein, used for the core layer. This core layer may optionally contain ethylene blended with the propylene polymer. This core layer is sandwiched between two ethylene polymer skin
5 layers. These skin layers may be comprised of LDPE, LLDPE, HDPE, substantially linear polyethylene, homogeneously branched linear polyethylene, and blends thereof.

Films made of the compositions of the invention advantageously have greater resistance to tear and puncture than films of the same gauge made by the same process but from the same coupled propylene polymer(s) without the ethylene polymer.
10 Preferably, films of the invention have a machine direction tear resistance (MD tear) as measured according to the procedures of ASTM D1922 of at least 5 g/mil (0.2 g/micron) preferably at least 7.5 g/mil (0.3 g/micron), a cross directional tear resistance (CD tear) as measured according to the procedures of ASTM D1922 of at least 20 g/mil (0.8 g/micron) preferably at least 50 g/mil (2 g/micron).

15 Surprisingly, blown films according to the current invention can be produced at higher output rates, higher haul-off rates, thinner film thicknesses, or a combination thereof.

Blown films comprising the propylene polymer/ethylene polymer blend according to the current invention have surprisingly been found to have better anti-
20 blocking characteristics than blown films made with either polymer alone.

Films made of the compositions of this invention advantageously have greater heat seal strength than films of the same gauge made from the same propylene polymers and ethylene polymers but without the coupling process.

25 ADDITIVES

Additives are optionally included in compositions of the invention. Additives are well within the skill in the art. Such additives include, for instance, stabilizers including free radical inhibitors and ultraviolet wave (UV) stabilizers, neutralizers, nucleating agents, slip agents, antiblock agents, pigments, antistatic agents, clarifiers,
30 waxes, resins, fillers such as silica and carbon black and other additives within the skill

in the art used in combination or alone. Effective amounts are known in the art and depend on parameters of the polymers in the composition and conditions to which they are exposed.

5 USES

These films are advantageously used to make institutional liners, that is liners (or trash bags) for trash cans used in industry. Characteristics useful in these liners are good tear, (dart) impact strength, puncture strength, and high modulus. The term “good” is used to indicate tear above 5g in the MD and 10 g in the CD measured by the tests listed in the previous paragraph, impact strength above 30 g/mil as measured by the modified procedure of ASTM D1709 condition A as described previously. The term “high modulus” is used to mean secant modulus as measured by ASTM D 882 of at least 40,000 psi (275,790 kPa). The liners and similar products are made for instance by processes within the skill in the art such as those disclosed by C.A. van Kerckhoven, et al, “Quality Performance Optimization Tools for the Fabrication of HMW-HDPE Blown Film”, Polymers, Laminations, & Coatings Conference, Book 2, 1990, pages 68-85.

The present invention includes but is not limited to use of the films of the invention in such applications as consumer liners, heavy duty shipping sacks, produce bags, batch inclusion bags, pouches, grocery bags, merchandise bags, bags for foam packaging (especially where the foam is formed in the bag), cereal liners, soft paper overwrap, multi-wall bags, baler bags, bundling films, compression films and laminations.

Films of the current invention are also useable as heat seal films, pouches or bags.

EXAMPLES

The following examples are to illustrate this invention and do not limit it. Ratios, parts, and percentages are by weight unless otherwise stated. Examples (Ex) of

the invention are designated numerically while comparative samples (C.S.) are designated alphabetically and are not examples of the invention.

The oxy bis(4-sulfonyl azide) benzene is prepared by the reaction of sodium azide with the corresponding bis(sulfonyl chloride) which is commercially available.

- 5 An aqueous solution of sodium azide is added to an acetone solution of the bis(sulfonyl chloride), and the product is isolated by precipitation with excess water.

COMPARATIVE SAMPLES A: FILMS FROM RANDOM PROPYLENE COPOLYMERS

10

a. Preparation of coupled isotactic polypropylene

- Isotactic polypropylene pellets (commercially available from Montell NA under the trade designation Profax SA861, which is a random copolymer of propylene and 2.5 weight percent of ethylene, melt flow rate (MFR) = 6.5 dg/min (230°C/2.16 kg)(ASTM D1238), commercially available from Montell USA Inc. is referred as Comparative Sample A:A.
- 15

- A 90800g sample of C.S. A:A was tumble blended with 2000 ppm of mineral oil at room temperature for 30 minutes followed by tumble blending with 1000 ppm each of phenolic and phosphite antioxidants commercially available from Ciba Geigy Corp. under the trade designations Irganox 1010 and Irgafos 168, respectively, and 200 ppm of oxy-bis(4-sulfonyl azide) benzene (hereinafter in the examples of this invention referred to as BSA) for an additional 30 minutes at room temperature. The resulting admixture was then fed into a 40 mm twin screw extruder with a temperature profile of 170, 180, 190, 200, 200, 210, 220, 230, 240, 240, and 240°C from the rear to the front of the extruder. The extruder had a die temperature of 240 °C to ensure the full reaction of the BSA and propylene polymer. The resulting melt-extruded polymer strand was run through a water cooling bath (at 19 °C) before it was pelletized by a pelletizer commercially available from Sheer Bay of Bay City, MI under the trade designation Sheer Pelletizer (Model # SGS100-E). The output rate for this extrusion
- 20
- 25
- 30

and pelletizing processes is 200 pounds/hr (90.8kg/hr). The resulting coupled material is referred to herein as the Comparative Sample A:B .

The procedure of Comparative Sample A:B was repeated except that 400 ppm BSA was used instead of 200 ppm BSA. This 400 ppm BSA coupled resin is referred to herein as the Comparative Sample A:C.

b. Blowing of film in LD/LLDPE extruder:

The resulting resins were then separately and independently fed to a blown film extruder having a screw diameter 2.5 inches (6.35 cm), 6 inches (15.24 cm) in die diameter, with a die gap of 30 mil (750 micron), die temperature 440 °F (226.7 °C), and blow up ratio (BUR) of 3.5, commercially available from Macro Engineering Company under the trade designation DC2900 and otherwise used according to manufacturer's directions. This blown film equipment is referred to herein as "LDPE/LLDPE" because it is commonly used to blow film from low or linear low density polyethylene. The extruder is 152.4 cm long and is kept at a temperature greater than 170 °C,. The so called "hump style temperature" profile (which means that the temperature is higher in the compressing section than both feed and metering sections) is used with a temperature of 190 °C in the feeding section, 225 °C in the compressing section and 215 °C in the metering section.

The resulting films are 0.35 mil (8.8 micron) gauge films were fabricated with random copolymer polypropylene Comparative Sample A:A, Comparative Sample A:B and Comparative Sample A:C at 3.5 BUR. The maximum output rates for each are 8.6 lb/h/in of die circumference (0.427 g/s/cm), 10.6 lb/h/in (0.527 g/s/cm), and 13.3 lb/h/in (0.658 g/s/cm) of die circumference for Comparative Samples A:A, A:B, and A:C, respectively, as shown in Table 2. Comparative Samples A:A, A:B and A:C demonstrate that the blown film extrusion output in the LD/LLDPE blown film line increased from a low rate of 8.6 lb/hr into a more commercially effective rate after reaction with 400 ppm of BSA.

**COMPARATIVE SAMPLES B: FILMS FORMED FROM PROPYLENE
IMPACT COPOLYMER**

Preparation of resins:

5 The preparation of coupled isotactic polypropylene procedure of Comparative Sample A:B was repeated except that an impact copolymer of propylene and 9 weight percent of ethylene, melt flow rate (MFR) =2 dg/min (230°C/2.16kg) (ASTM 1238, condition D at 230°C) commercially available from The Dow Chemical Company under the trade designation INSPiRE C105-02 (and referred to herein as Comparative
10 Sample B:A) was used instead of the polymer used in C.S. A:B and 350 ppm BSA was used instead of 200 ppm BSA. The resulting polymer coupled using 350 ppm BSA is herein referred as Comparative Sample B:B having the properties shown in Table 2.

Blowing of films with high stalk HDPE extruder

15 The resulting resins were then fed to blown film equipment that is commonly used for high molecular weight high density polyethylene (HDPE), in place of the LDPE/LLDPE type of equipment used in Example 1. The equipment has a screw diameter 2 inches (50mm), 6 inches (150mm) in die diameter, die gap of 40 mil (1000 microns), die temperature 425 °F (218.3°C), and a blow up ratio (BUR) of 3.5. The
20 equipment is commercially available from Alpine, Inc under the trade designation model # HS50R and is designated in the table as "HDPE."

 The resulting 1.0 mil (25 micron) gauge films were fabricated using 2 MFR impact copolymer polypropylene polymer (Comparative Sample B:A), and Comparative Sample B:B at 3.5 BUR. The blown film extrusion rate for Comparative
25 Sample B:B is 6.37 lb/h/in (0.316 g/s/cm) of die circumference in this high stalk line. However, it was not possible for Comparative Sample B:A to form a stable bubble at 4.24 lb/h/in (0.211 g/s/cm) of die circumference, as shown in Table 2. The 4.24 lb/h/in of die circumference is the minimum output rate that this extruder can deliver. Comparative Sample B demonstrated that reaction of the polymer of C.S. B with 350

ppm of BSA greatly increases the effective film fabrication rate in the high stalk HDPE blown film line.

**COMPARATIVE SAMPLES C: EFFECTS OF BLENDING POLYETHYLENE
WITH A PROPYLENE HOMOPOLYMER.**

a. On-line blending

A homopolymer polypropylene commercially available from Montell USA Inc. under the trade designation Pro-fax H300-02Z has a melt flow rate of 2.0 dg/min (230°C/2.16 kg) [ASTM D1238], is referred to herein as Comparative Sample C:A. Pellets of C.S. C:A were vacuum conveyed into one of the feeders in the LD/LLDPE extruder described in C.S. A by a vacuum pump via a flexible hose. Pellets of a linear low density polyethylene commercially available from The Dow Chemical Company under the trade designation DOWLEX 2045 having a melt flow rate (MFR according to the procedure of ASTM 1238, condition D of 3.0, a flex modulus (according to the procedure of ASTM D790A of 26000 psi (1.79 X10⁵ kPa) an Izod impact strength according to ASTM D256A of "no break" and a melt strength according to the procedures of ASTM D 3568 # 2 of 4.0 cN (centiNewtons). were conveyed into the hopper in the LD/LLDPE extruder by vacuum pump via flexible hose. Controlled by electronic device, 85 percent of C.S. C:A and 15 percent of the polyethylene were gravitically fed from the hopper into the extruder. The resulting blend is referred to herein as Comparative Sample C:B. The same polyethylene is used in each instance where a polyethylene is used in any subsequent Comparative Samples or Examples unless stated otherwise.

The procedure of C.S. C:B is repeated using 25 weight percent of the same polyethylene and 75 percent of the same polypropylene as in C.S. C:B. and the resulting blend is referred to herein as Comparative Sample C:C.

The blown film line used in this Comparative Sample is the same as the one that was described in Comparative Sample A. Films were fabricated with these three resins at 3.5 BUR, 120 lb/h of output rate (54.54 kg/h) and 0.75 mil (17.5 micron) gauge. Selected properties for these films are listed in Table 3. It can be seen from Table 3

that film properties are greatly improved by adding 25 percent of polyethylene. The data in Table 3 demonstrates the result of blending polyethylene with a polypropylene homopolymer on film properties.

5 **COMPARATIVE SAMPLE D: EFFECTS OF BLENDING POLYETHYLENE
WITH A RANDOM PROPYLENE COPOLYMER.**

 The procedure of Comparative Sample C was repeated except that a random copolymer commercially available from Montell USA, Inc. under the trade designation Pro-fax SR-256M (designated C.S. D:A herein) having properties described in C.S. D:A was used instead of C.S. C:A. Selected properties of C.S. D:A are presented in
10 Table 3 for the resulting films. It can be seen from the data in Table 3 that both MD- and CD-tear and dart impact strength have been significantly improved after blending 25 percent of the polyethylene used in C.S. C. This demonstrates the effect on film properties of blending polyethylene with a random propylene copolymer.

15

**COMPARATIVE SAMPLE E: EFFECTS OF BLENDING POLYETHYLENE
WITH AN IMPACT PROPYLENE COPOLYMER.**

 The procedure of Comparative Sample C was repeated except that an impact copolymer commercially available from The Dow Chemical Company under the trade
20 designation INSPiRE C105-02 (designated C.S. E:A) having properties described in C.S. B:A was used instead of C.S. C:A. Selected properties are presented in Table 3 for the resulting films. It can be seen from the Table that both MD- and CD-tear strength have been significantly improved after blending 25 percent polyethylene with the impact propylene copolymer.

25

**EXAMPLE 1 AND COMPARATIVE SAMPLE F: FILMS OF BLENDS OF
COUPLED POLYPROPYLENE AND POLYETHYLENE**

The preparation of coupled isotactic polypropylene procedure described in Comparative Sample A was repeated except that a random copolymer polypropylene
5 commercially available from Montell USA Inc. under the trade designation Pro-fax SR-256M having properties of in Table 1 was used instead of the polypropylene of C.S. A and the BSA level was 500 ppm instead of 200 ppm. The resulting coupled polypropylene is referred to herein as Comparative Sample F. A portion of the C.S. F material was blended with the polyethylene used in C.S. C in an amount corresponding
10 to 25 percent of the resulting blend using the on-line blending method described in Comparative Sample C and is referred to herein as the Example 1. These two materials C.S. F and Ex 1 were fabricated with LD/LLDPE blown film equipment as described in Comparative Sample A. Selected properties for these films are listed in Table 4. It can be seen from Table 4 that adding 25 percent of polyethylene significantly improves dart
15 impact, tear and puncture resistances demonstrating the effect on the film properties of adding polyethylene to coupled random copolymer polypropylene film made on LD/LLDPE blown film equipment.

**EXAMPLE 2 AND COMPARATIVE SAMPLE G: FILMS OF BLENDS OF
20 COUPLED IMPACT COPOLYMER POLYPROPYLENE AND
POLYETHYLENE**

The preparation of coupled isotactic polypropylene procedure described in Comparative Sample A was repeated except that the impact copolymer polypropylene used in C.S. B was used instead of the polypropylene of C.S. A and the BSA level was
25 300 ppm instead of 200 ppm. The resulting coupled polypropylene is referred to herein as Comparative Sample G. A portion of the C.S. G material was blended with the polyethylene used in C.S. C in an amount corresponding to 15 percent of the resulting blend using the on-line blending method described in Comparative Sample C and is referred to herein as the Example 2. In that method, 42.5 lbs (19.3 kg) of Comparative
30 Sample G material and 7.5 lb (3.4 kg) of the polyethylene of C.S. C were weighted and

put into a plastic drum liner which was then placed in a 30 gallon fiber drum such that there is a void space to allow free tumbling of the contents. The fiber drum was then placed in a mechanical blender and tumble blended for 30 minutes at room temperature. The resulting material is a mixture of C.S. G with 15 percent of polyethylene and is referred to herein as Example 2.

Samples of C.S. G and Ex 2 were separately and independently fed by vacuum conveying to a blown film extruder having a screw diameter 2.0 inches (5.08 cm), 3 inches (7.62 cm) in die diameter, with a die gap of 30 mil (750 micron), die temperature 440 F (226.7 °C), and blow up ratio (BUR) of 3.0, commercially available from Egan Corporation under the trade designation model B00G345. This blown film equipment is referred to herein as "LDPE/LLDPE" equipment because it is commonly used to blow film from low or linear low density polyethylene. The extruder is 121.9 cm long and is kept at a temperature greater than 170 °C. The so called "hump style temperature" profile used with a temperature of 190 °C in the feeding section, 225 °C in the compressing section and 215 °C in the metering section. The output rate was 2.65 lb/h/in (0.132 g/s/cm) of die circumference. Selected properties for these films are listed in Table 4. It can be seen from Table 4 that adding 15 percent of polyethylene significantly improves dart impact, tear and puncture resistances demonstrating the effect on the film properties of adding polyethylene to coupled impact copolymer polypropylene film made on LD/LLDPE blown film equipment.

EXAMPLE 3 AND COMPARATIVE SAMPLES H AND I: FILMS OF BLENDS OF COUPLED IMPACT COPOLYMER POLYPROPYLENE AND POLYETHYLENE

The preparation of coupled isotactic polypropylene procedure described in Comparative Sample A was repeated except that the polypropylene used in C.S. B was used instead of the polypropylene used in C.S. A and the BSA level was 500 ppm instead of 200 ppm. The resulting coupled material is referred to herein as Comparative Sample H. A portion of the Comparative Sample H material was blended with the polyethylene used in C.S. C and the polypropylene used in C.S. B by the on-line

blending method as described in Comparative Sample C. The resulting material has a composition of 64 percent Comparative Sample H, 20 percent Comparative Sample B:A, and 16 percent polyethylene and is referred to herein as Example 3 (the ratio of C.S. H/C.S. B:A is 76/24). Another portion of Comparative sample H was blended with 24 percent C.S. B:A by the on-line blend method. The resulting material has a composition of 76 percent Comparative Sample H and 24 percent Comparative Sample B:A. and is referred to herein as Comparative Sample I. in Table 4 the amount of BSA is listed as 380 ppm which is the concentration based on the weight of both propylene polymers even though one propylene polymer (C.S. H) was treated with 500 ppm BSA and the other (C.S. B:A) was not coupled with BSA. Similar averaging was done to represent the other examples with more than one propylene polymer listed in Table 4.

These two materials (Ex 3 and C.S. I) were fabricated separately and independently using the LD/LLDPE blown film equipment as described in Comparative Sample C. Selected properties for these films are listed in Table 4. It can be seen from Table 4 that adding 16 percent of polyethylene significantly improves tear and puncture resistances. This example demonstrates the effect on the film properties adding polyethylene to coupled impact copolymer polypropylene in film made using LD/LLDPE blown film equipment.

EXAMPLE 4 AND COMPARATIVE SAMPLE J: FILMS OF BLENDS OF COUPLED IMPACT COPOLYMER POLYPROPYLENE AND POLYETHYLENE

A portion of the Comparative Sample H material (as prepared by the procedure of Example 3) was blended with the polyethylene used in C.S. C and C.S. B:A by the tumble blending method as described in Example 2. The resulting material has a composition of 64 percent Comparative Sample H, 20 percent Comparative Sample B:A and 16 percent polyethylene and is referred to herein as the Example 4 (the ratio of C.S. H/C.S. B:A is 76/24). Another portion of Comparative Sample H was blended with 24 percent of the polypropylene C.S. B:A by the tumble blending method. The resulting material has a composition of 76 percent Comparative Sample H and 24

percent Comparative Sample B:A and is referred to herein as the Comparative Sample J.

The materials of Ex 4 and C.S. J were fabricated using a high stalk HDPE blown film as described in Comparative Sample B. Selected properties for these films are listed in Table 4. It can be seen from Table 4 that adding 16 percent of polyethylene improves tear resistance. This example demonstrates the effect on the film properties of adding polyethylene to coupled impact copolymer polypropylene in film formed using high stalk HDPE blown film equipment.

10 EXAMPLES 5-7 AND COMPARATIVE SAMPLES K: OUTPUT RATE COMPARISONS

Blown film was fabricated on a Gloucester blown film line comprised of the following collection of equipment:

- 2.5 in. 24:1 L/D extruder
- 15 2.5 in. diameter, single flight, double mixing section screw
- 6 in. diameter, Gloucester die, with 40 mil die pin.
- Saturn dual lip air ring
- Tower, nip rolls, Gloucester dual turret winder.
- Blow-up-ratio is 2.5:1, giving a layflat width of 23.5 in.
- 20 Film was produced from Montell 7723, a 0.8 dg/min (230°C/2.16 kg), propylene impact copolymer, procured from Montel. Fabrication conditions included:
 - Screw speed of 67.7 rpm
 - Output rate of 120 lb/hr
 - Melt temperature of 480F
 - 25 Extruder back pressure of 4650 psi.

At these conditions, the haul-off rate was increased as far as possible to reduce the thickness of the film and to determine the minimum thickness or maximum haul-off rate at which a stable bubble could be maintained and film could be controllably fabricated. For 100 percent Montell 7723 (C.S. K:A), the limit was found to be 95

ft/min haul-off rate or a thickness of around 1.5 mil. At that point the bubble starts wandering around the air ring and can no longer be controlled or locked in.

A similar trial was conducted, but this time with a blend of 65 percent Montell 7723 and 35 percent of a 0.5 MI, 0.918 density ethylene-octene copolymer, produced using a Ziegler-Natta catalyst system (C.S. K:B). The minimum thickness for the blend was 1.3 mils.

A 0.8 MFR propylene impact copolymer, very similar to Montell 7723, was treated with 200 ppm BSA (EX. 5). This rheology-modified resin was fabricated into film under similar conditions on the same equipment as the above trial. Fabrication conditions included:

Screw speed of 69 rpm

Output rate of 120.8 lb/hr

Melt temperature of 480 F

Extruder back pressure of 3790 psi

At these conditions, the haul-off rate was increased as far as possible to reduce the thickness of the film and to determine the minimum thickness or maximum haul-off rate at which a stable bubble could be maintained and film could be controllably fabricated. For EX. 5, the maximum rate was 250 fpm and a thickness of 0.5 mil. Much higher rates and thinner film could be achieved for EX. 5 than was possible with either C.S. K:A or K:B.

A similar trial was conducted, but this time with a blend of 65 percent of the resin of EX. 5 and 35 percent DOWLEX 2045 (1.0 MI, 0.920 density, ethylene-octene copolymer available from The Dow Chemical Company)(EX. 6). With the blend of materials, it was again possible to reach a haul-off rate of 250 ft/min. and a thickness of 0.5 mil. Conditions for this trial included:

Screw speed of 62.1 rpm

Output rate of 119.4 lb/hr

Melt temperature of 463 F

Extruder back pressure of 3770 psi.

Likewise, a film was fabricated from a blend of 65 percent DP836, (a 0.5 MFR, ethylene-propylene, random copolymer (~3.5 percent ethylene) produced in Safripol) and 35 percent of the ethylene-octene copolymer used for C.S. K:B (C.S. K:C). The bubble was very unstable and output rates had to be slowed to 100 lb/hr. At this rate,
5 the minimum thickness that could be obtained was approximately 2.5 mil.

Next, a sample of DP836, treated with 150 ppm BSA, blended with 35 wt. percent of the ethylene-octene copolymer used for C.S. K:B was evaluated (EX. 7). Thin film down to 0.5 mil could be fabricated without difficulty.

These trials show that treatment with BSA improves the ability to fabricate thin
10 films at high drawn-down speeds. The results of these trials are shown in Table 5.

EXAMPLES 8-10 AND COMPARATIVE SAMPLES L AND M: BLOCKING COMPARISONS

A rheology modified propylene impact copolymer was produced as described
15 for Example 5. This modified propylene ICP was blended with an LDPE (DOWLEX 2045) in weight percentages of polypropylene of 0, 50, 70, 85 and 100 percent (based on the weight of the combined polymers) to form C.S. L, Example 8, Example 9, Example 10, and C.S. M, respectively. Blown film was fabricated from these blends on a Gloucester blown film line as described for Example 5. The average blocking was
20 determined for each sample and the results are shown in Table 6. As shown in Table 6, the examples of the inventive blend of modified polypropylene impact copolymer and polyethylene had a lower average block than did either polymer alone. These results were particularly noticable at higher polypropylene weight percentages (Examples 9 and 10) where the average block was less than half the average block for either polymer
25 alone.

EXAMPLE 11 AND COMPARATIVE SAMPLE N:

Trials were conducted comparing a base random copolymer (RCP)(PROFAX SA861, available from Montell(C.S.N)) versus a coupled high melt strength random
30 copolymer (HMS RCP)(PROFAX SA861 coupled by reaction with 200 ppm BSA(EX.

11)). The heat seal performance of 0.4 and 0.7 ml monolayer films of the base RCP and the HMS RCP are shown in Figure 1. Ultimate heat seal strength of the HMS RCP, in both the thin and thicker films, is approximately 25 percent higher than the base RCP. Similar trends are seen for homopolymers and impact copolymers.

5

EXAMPLE 12 AND COMPARATIVE SAMPLE O:

The coupled propylene polymers used in this invention provide significant processing advantages. Trials were run using a coupled propylene impact copolymer as described for Example 3. As shown in Figure 2, the coupled propylene impact
10 copolymer (EX. 12) provides lower back pressure than a high molecular weight high density polyethylene (C.S. O) when extruded on a linear low density polyethylene line. The trials shown in Figure 2 were run at 120 lbs./hr. using a 70 ml. die gap with a 6 inch die.

15 Likewise, use of coupled propylene impact copolymers provides for maximum output rates when compared against linear low density polyethylene. Trials were conducted on an LLDPE line with a 70 ml. die gap, a 6 inch die and drawing film to a 0.6 mil gauge. The maximum sustainable output rate was measured and is plotted on Figure 3. The high melt strength ICP is the same as used for Example 3. The LLDPE
20 is an ethylene polymer having a density of 0.920 g/cm³ and a melt index of 0.5 (available under the trade name Dowlex 61528.20).

Table I: Starting Material Propylene Polymers

Identity herein	Weight percent propylene	Weight percent other monomers specified	Melt flow rate (MFR) in dg/min (230°C/2.16 kg) by the procedures of ASTM 1238	Flex Modulus psi (kPa) measured by the procedures of ASTM 790A at condition D	Izod Impact in ft-lb/in (J/m) measured by the procedures of ASTM 256A at condition D	Tensile strength psi (kPa) measured by the procedures of ASTM 638 at condition D	Melt Strength in centiNewtons (cN) measured by the procedures of ASTM
Comparative Sample A:A	97.5 percent	2.5 percent	6.5	130,000 (8.96E5)	1.1 (58.68)	4000 (27,579)	1.1
Comparative Sample B:A	82 percent	18 percent	2.0	140,000 (9.65E5)	No break	3200 (22,060)	4.5
Comparative Sample C:A	100	0	2.0	230,000 (1.59E6)	0.8 (42.77)	5000 (34,500)	4.0
Comparative Sample D:A	96.8 percent	3.2 percent	2.0	15,000 (1.06E6)	6.0 (320)	4000 (27,579)	4.0

Table 2: Comparative Samples Showing the Effects of Coupling on Output Rate

Identity herein	Ppm by weight BSA	Melt flow rate (MFR) dg/min (230°C/2.16 kg) by the procedures of ASTM D1238	Flex Modulus psi (kPa) measured by the procedures of ASTM D790A	Izod Impact in ft-lb/in (m-kJ/m) measured by the procedures of ASTM D256A	Tensile strength psi (kPa) measured by the procedures of ASTM D638	Melt Strength in centiNewtons (cN) measured by the procedures of ASTM	Type of blown film equipment used as described herein (HDPE or LLDPE/LDPE)	Maximum output without bubble breaking in lb/hr (kg/hr)
Comparative Sample A:A	0	6.5	130,000 (8.96E5)	1.1 (58.68)	4000 (27,579)	1.1	LLDPE/LDPE	162 (73.6)
Comparative Sample A:B	200	4.4	N/A	N/A	N/A	10.5	LLDPE/LDPE	200 (90.9)
Comparative Sample A:C	400	2.8	N/A	N/A	N/A	13.5	LLDPE/LDPE	245 (111.4)
Comparative Sample B:A	0	2.0	140,000 (9.65E5)	No break	3200 (22,060)	4.5	HDPE	< 90 (< 40.9)
Comparative Sample B:B	350	0.7	N/A	N/A	N/A	45	HDPE	120 (54.5)

Table 3: Comparative Samples Showing Impact of Blending Polyethylene on Films

Identity herein	Ppm by weight BSA	Blended with weight percent polyethylene	Gauge in mil (m) of film	MD tear g/mil (g/m) measured by the procedures of ASTM D1922	CD tear g/mil (g/m) measured by the procedures of ASTM D1922	CD elongation percent measured by the procedures of ASTM D882	Dart impact g/mil (g/m) measured by the procedures of ASTM D1709 at condition A except as noted	CD toughness ft-lb/in ³ (Newton/m ³) measured by the procedures of ASTM	Type of blown film equipment used as described herein (HDPE or LLDPE/LDPE)	Rate of production lb/hr (kg/hr) at 3.5 BUR unless noted otherwise
Comparative Sample C:A	0	0	0.75	6.5	27.4	11		29	LLDPE/LDPE	120 (54.5)
Comparative Sample C:B	0	15	0.75	9.3	42	10		29	LLDPE/LDPE	120 (54.5)
Comparative Sample C:C	0	25	0.75	12.9	130	670		2240	LLDPE/LDPE	120 (54.5)
Comparative Sample D:A	0	0	0.75	3.6	18.5		*139		LLDPE/LDPE	120 (54.5)
Comparative Sample D:B	0	15	0.75	9.9	28.7		*139		LLDPE/LDPE	120 (54.5)
Comparative Sample D:C	0	25	0.75	11.4	127		*199		LLDPE/LDPE	120 (54.5)
Comparative Sample E:A	0	0	0.75	12.3	32.2		66		LLDPE/LDPE	120 (54.5)
Comparative Sample E:B	0	15	0.75	11.7	95.5		90		LLDPE/LDPE	120 (54.5)
Comparative Sample E:C	0	25	0.75	19.9	137		72		LLDPE/LDPE	120 (54.5)

Table 4: Examples 1-4 in films

Identity herein	Ppm by weight BSA	Blended with weight percent polyethylene	Gauge in mil (mm) of film	MD tear g/mil (g/m) measured by the procedures of ASTM D1922	CD tear g/mil (g/m) measured by the procedures of ASTM D1922	CD elongation percent measured by the procedures of ASTM D882	Dart impact g/mil (g/m) measured by the procedures of ASTM D1709 at condition A except as noted	CD toughness lb/in ³ (Newton/m ³) measured by the procedures of ASTM D882	Puncture ft-lb/in ³ (Newton/m ³) measured by the procedures of ASTM 1709 except that the dart is dropped from 10.5" (0.27m)	Type of blown film equipment used as described herein (HDPE or LLDPE/ LDPE)	Rate of production lb/hr (kg/hr) at 3.5 BUR unless noted otherwise
Comparative Sample F	500	0	1.0 (0.025)	7.7	13.7	11.0	66.0*	30.0	70.0	LLDPE/ LDPE	120 (54.5)
Example 1	500**	25	1.0 (0.025)	14.8	73.9	690.0	232*	2090.0	100.0	LLDPE/ LDPE	120 (54.5)
Comparative Sample G	300	0	1.0 (0.025)	4.7	27.1		32.5		81.8	LLDPE/ LDPE	25 lb/h (11.36 kg/h) at 3.0 BUR
Example 2	300**	15	1.0 (0.025)	7.9	45.4		52.5		99.4	LLDPE/ LDPE	25 lb/h (11.36 kg/h) at 3.0 BUR
Comparative Sample I	380***	0	1.0 (0.025)	7.3	29		65		88	LLDPE/ LDPE	120 lb/h (54.5 kg/h) at 3.5 BUR
Example 3	380**	16	1.0 (0.025)	17	48		66		102.5	LLDPE/ LDPE	120 lb/h (54.5 kg/h) at 3.5 BUR
Comparative Sample J	380**	0	1.0 (0.025)	7.6	8.8					HDPE	100 lb/h (45.45 kg/h) 3.5 BUR
Example 4	380**	16	1.0 (0.025)	10.6	30.8					HDPE	100 (45.45 kg/h) 3.5 BUR

* In these instances, Dart impact strength was measured according to ASTM D1709 except the height of the dart is 10.5" instead of 26".

** In these instances, the amount of BSA is the amount of BSA in the polypropylene resin.

*** In these instances, the amount of BSA is averaged between BSA coupled and uncoupled polypropylene resins.

Table 6 - Blocking Comparisons

SAMPLE	C.S.L.	Ex. 8	Ex. 9	Ex. 10	C.S.M.
Coupled Propylene ICP (wt. percent)	0	50	70	85	100
Average Block	69.24	8.64	5.04	5.02	12.5

These examples show that reacting BSA with polypropylene improves the blown film
5 fabrication rate achievable, reduces the minimum gauge attainable, and/or increases the
maximum haul-off rate or line speed achievable. In addition blending polyethylene
enhances the film properties regardless of the equipment used.

We Claim

1. A composition comprising

(a) at least one propylene polymer coupled by reaction with a coupling amount of poly(sulfonyl azide) sufficient to increase the melt strength of the resulting coupled propylene polymer to at least 1.5 fold that of the propylene polymer before coupling; and

(b) at least one ethylene polymer

wherein the ethylene polymer is present in an amount sufficient to improve film mechanical properties of tear resistance in either the machine direction (MD) and cross direction (CD) as measured by the Elmendorf Tear method (ASTM D-1922) or dart impact strength as measured by the procedure of ASTM D-1709 or a modified method thereof in which the height from which the dart is dropped is decreased from 26" to 10.5" (0.66m to 0.27m) as compared with a film formed in the same manner using the coupled propylene polymer of (a) alone.

2. The composition of Claim 1 wherein the propylene polymer is coupled by a process comprising a step of (a) heating a mixture of the propylene polymer and a rheology modifying amount of a poly(sulfonyl azide) to a temperature, referred to hereafter as a reaction temperature, which is at least the decomposition temperature of the poly(sulfonyl azide).

3. The composition of Claim 1 wherein the poly(sulfonyl)azide is selected from 1, 5-pentane bis(sulfonyl azide), 1,8-octane bis(sulfonyl azide), 1,10-decane bis(sulfonyl azide), 1,10-octadecane bis(sulfonyl azide), 1-octyl-2,4,6-benzene tris(sulfonyl azide), 4,4'-diphenyl ether bis(sulfonyl azide), 1,6-bis(4'-sulfonazidophenyl)hexane, 2,7-naphthalene bis(sulfonyl azide), oxy-bis(4-sulfonylazidobenzene), 4,4'-bis(sulfonyl azido)biphenyl, bis(4-sulfonyl azidophenyl)methane, mixed sulfonyl azides of chlorinated aliphatic hydrocarbons containing an average of from 1 to 8 chlorine atoms and from 2 to 5 sulfonyl azide groups per molecule, and mixtures thereof.

4. The composition of Claim 1 wherein the poly(sulfonyl azide) is used in an amount greater than 0.01 and less than 0.3 weight percent based on the total weight of the propylene polymer.
5. The composition of any of Claims 1-4 wherein the propylene polymer is present in an amount of greater than 50 weight percent of the resulting composition and the ethylene polymer is present in an amount of from 5 to 49 weight percent.
6. The composition of any of Claims 1-5 wherein the amount of ethylene polymer is from 10 to 40 weight percent of the resulting composition.
7. The composition of any of Claims 1-6 wherein the amount of ethylene polymer is from 15 to 35 weight percent of the resulting composition.
8. The composition of any of Claims 1-7 wherein the ethylene polymer is a low density polyethylene, linear low density polyethylene, substantially linear polyethylene, homogeneously branched linear polyethylene, or a blend thereof.
9. The composition of any of Claims 1-8 wherein the ethylene polymer has a density of from 0.865 g/cm³ to 0.96 g/cm³.
10. The composition of any of Claims 1-8 wherein the ethylene polymer has a density of from 0.88 g/cm³ to 0.930 g/cm³.
11. The composition of any of Claims 1-10 wherein the ethylene polymer is a substantially linear polyethylene.
12. The composition of any of Claims 1-11 wherein the propylene polymer is isotactic.
13. The composition of any of Claims 1-11 wherein the propylene polymer is a homopolymer.
14. The composition of any of Claims 1-11 wherein the propylene polymer is a random copolymer of propylene and a comonomer.
15. The composition of any of Claims 1-11 wherein the propylene polymer is an impact copolymer of propylene and at least one comonomer.

16. The composition of any of Claims 1-11 wherein the propylene polymer is a random copolymer of propylene and at least one comonomer comprising ethylene.
17. The composition of any Claim 15 or 16 wherein the propylene polymer is a copolymer of propylene and at least one comonomer other than ethylene.
18. The composition of any of Claims 1-17 that can be extruded on both high and low stalk extruders.
19. A blown film of a composition of any of Claims 1-18.
20. The blown film of Claim 19 blown on a high stalk blown film extruder.
21. The blown film of Claim 19 blown on a low stalk blown film extruder.
22. The blown film of any of Claims 19-21, which is a coextruded film.
23. The blown film of any of Claims 19-21, which is a monolayer film.
24. A process of blowing a film of a composition of any of Claims 1-18.
25. The process of Claim 24 wherein the film is blown using a high stalk extruder.
26. The process of Claim 24 wherein the film is blown using a low stalk extruder.
27. The process of Claim 24 wherein the film is blown using a coextruder.
28. An article comprising a composition of any of Claims 1-18 or a film of any of Claims 19-23.
29. The article of Claim 28 which is an institutional liner, consumer liner, heavy duty shipping sack, produce bag, batch inclusion bag, pouch, grocery bag, merchandise bag, packaging, cereal liner, soft paper overwrap, multi-wall bag, lamination or combination thereof.
30. The article of Claim 28 or 29 having a multiwall configuration.
31. The article of any of Claims 28-30 having a multilayer configuration.
32. A use of a composition of any of Claims 1-18 as a starting material for making a blown film.

33. The blown film of any of claims 19-23, wherein the poly(sulfonyl azide) is used in an amount greater than 0.01 and less than 0.3 weight percent based on the total weight of the propylene polymer present.
34. The composition of any of Claims 1-18 which is capable of being converted into a blown film at output rates at least 50 percent greater than a similar polymer composition wherein the propylene polymer is not coupled.
35. The composition of any of Claims 1-18 which is capable of being converted into a blown film at film haul off rates at least 50 percent greater than a similar polymer composition wherein the propylene polymer is not coupled.
36. A coextruded film comprising:
- (a) at least one layer comprising at least one coupled propylene polymer coupled by reaction with a poly(sulfonyl azide) to increase the melt strength of the coupled propylene polymer to at least 1.5 fold that of the propylene polymer before coupling; and
 - (b) at least one layer comprising at least one ethylene polymer.
37. The film of Claim 36, having at least one core layer comprising component (a) sandwiched between at least two outer layers, wherein the outer layers comprise component (b).
38. The film of Claim 36, having at least one core layer comprising component (b) sandwiched between at least two outer layers, wherein the outer layers comprise component (a).
39. The film of Claim 36, which is a heat sealable film.
40. The film of Claim 36, wherein component (a) is further comprised of at least one ethylene polymer
41. The film of Claim 40, wherein the at least one ethylene polymer comprising component (a) is selected from the group consisting of: LDPE, LLDPE, HDPE, substantially linear polyethylene, homogeneously branched linear polyethylene, and blends thereof.

42. The film of Claim 37, wherein the at least one ethylene polymer comprising component (b) is selected from the group consisting of: LDPE, LLDPE, HDPE, substantially linear polyethylene, homogeneously branched linear polyethylene, and blends thereof.
- 5 43. The film of Claim 42, wherein component (a) further comprises at least one ethylene polymer selected from the group consisting of LDPE, LLDPE, HDPE, substantially linear polyethylene, homogeneously branched linear polyethylene, and blends thereof.
- 10 44. The film of Claim 43, wherein the at least one ethylene polymer comprising component (a) is LLDPE.
45. The film of any of claims 36-44, wherein the poly(sulfonyl azide) is used in an amount greater than 0.01 and less than 0.3 weight percent based on the total weight of the propylene polymer present.

FIG. 1

Heat Seal Strength HMS PP Films

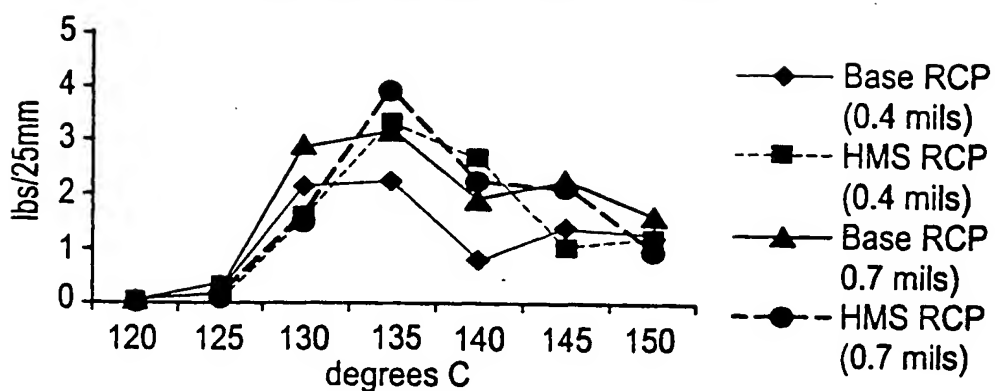


FIG. 2

Back Pressure Comparison

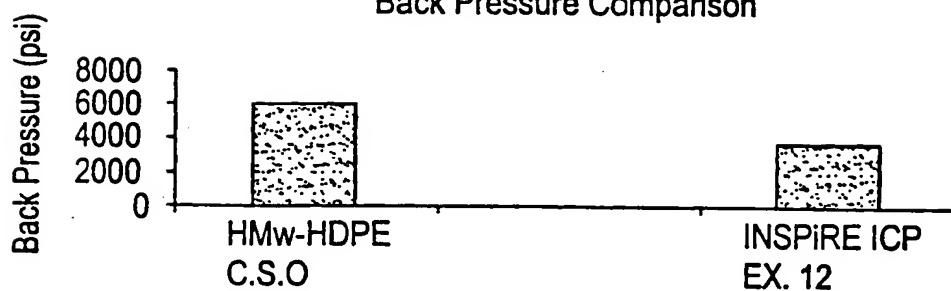
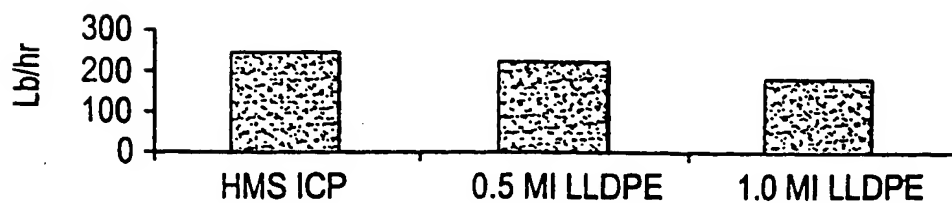


FIG. 3

Maximum Output Rate Comparison



INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/17320

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08L23/10 C08L23/04 C08F8/34 C08K5/43

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08F C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 336 268 A (WILLIAM W. COX) 15 August 1967 (1967-08-15)	1-7, 12-18, 28-35 36-40, 45
Y	claims; examples 37, 38	
X	WO 99 10426 A (MULLINS MICHAEL J ; HO THOI H (US); CUMMINS CLARK H (US); DOW CHEMI) 4 March 1999 (1999-03-04)	1-7, 12-21, 23-26, 28, 29, 32-35, 45 8-11, 22, 27, 30, 31, 36-44
Y	page 2, line 22 - line 23; claims 1, 2, 8, 10	
Y	EP 0 474 376 A (GRACE W R & CO) 11 March 1992 (1992-03-11) cited in the application claims	8-11, 22, 27, 30, 31, 36-45

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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G document member of the same patent family

Date of the actual completion of the international search

3 October 2000

Date of mailing of the international search report

17/10/2000

Name and mailing address of the ISA
European Patent Office, P.O. 5818 Patentean 2

Authorized officer

INTERNATIONAL SEARCH REPORT

Information on patent family members

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